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EVOLUTIONARY AND GEOLOGIC CONSEQUENCES OF ORGANIC CARBON FIXING IN THE PRIMITIVE ANOXIC OCEAN

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Abstract

A model is proposed for a group of Archean pre-prokaryotes primary producers (termed Anoxium), that derived their energy from geothermal hydrogen sulfide discharged at oceanic vents. With time, competition developed for available $S^=$ due to organic oxidation and loss of sulfur to sediments. As a consequence, evolutionary advantage shifted to Anoxium isolates that could use alternative energy sources such as light to supplement diminished supplies of $S^=$. Subsequent carbon fixing and deposition of organic carbon improved both the quality and quantity of light reaching the ocean surface so that eventually photosynthesis replaced sulfur chemosynthesis as the primary carbon dioxide-fixing mechanism. Organisms occupying niches similar to those of modern purple and green sulfur bacteria, thiobacilli and cyanobacteria could have evolved from the Anoxium complex as the environment was organically modified by the consequences of carbon fixing.

INTRODUCTION

The abundance of metazoan and microbial life about the Galapagos and other deep thermal springs [1,2,3,4,5,6,7] and analyses of the biological interrelationships about these springs suggests that geothermally produced hydrogen sulfide is the basic energy source used by chemoautotrophic bacteria to fix carbon dioxide. These bacteria appear to comprise the base of the food web about the springs [5].

Probable Archean analogs of these deep ocean thermal vents about which life abounds occur in the Canadian and African shields.[8,9] Cameron and Garrels[8] described certain Archean greenstone belts in the Canadian Shield in which graphitic layers occur "within or near" volcanic sequences. Anhaeusser and others[9] recorded the presence of carbonaceous layers interbedded with sedimentary and volcanic rocks in the older Archean Onverwacht and Fig Tree Series in southern Africa. These rock sequences appear to have formed near deep ocean volcanic activity.[9] Cameron and Garrels[8] pointed out that graphitic sediments in the Canadian Shield Archean greenstone belts "are frequently related stratigraphically to the sites of volcanic exhalations." They[8] noted the association of relatively high amounts of carbon and sulfur in Archean greenstone belt samples and suggested that that association "may be because the sites where volcanic exhalations entered the sea were particularly suitable for organic growth." They[8] suggested that "bacteria that utilize the oxidation of S compounds" could have flourished in such an environment, and that "hot sulphur springs of Archean time may have been the equivalent of today's tropical rain forest."

The coincidence of non-photosynthetic bacterial activity about modern deep ocean vents and the geologic record of apparently similar activity in the early phases of earth's development suggests that life could have originated in the form of chemoautotrophic bacteria that used geothermally produced hydrogen sulfide as the primary energy source to fix carbon dioxide. The free energy relationships among chemoautotrophic organisms and the free energies involved in oxidations of sulfur[10] suggests that, although available free energies are low, the free energy derived from use of hydrogen sulfide as an energy source in chemosynthesis could permit the reactions proposed herein to fix carbon dioxide.

MODEL OF PRIMITIVE LIFE

A model for structurally simple, probable pre-prokaryote organisms is developed from geologic, oceanographic, and environmental data. The steps in the model seem to be consistent with prokaryote evolution and pre-prokaryote history suggested by Fox and others[11] and Woese and Fox[12], based upon analysis of ribosomal RNA sequences. The model differs from certain others[13,14] in substituting anerobic chemoautotrophs for anerobic heterotrophs as primordial ancestors.

The pre-biotic conditions included an anoxic ocean[15] and a reducing atmosphere with a high carbon dioxide content. Hydrogen sulfide from volcanic vent outgassing would have persisted in an anoxic, acidic ocean because of its relatively high solubility[16]. Atmospheric and ocean temperatures would have been warm to hot, primarily as a consequence of the greenhouse effect. The quality of light at the sea surface would have been poor because cloudiness would have been persistent. Volcanic activity and erosion of crustal rocks could result in dissolved nitrogen compounds and phosphates in the ocean.[17] Under these conditions, chemoautotrophes that used $S^{=}$ as an electron source could form. This ancient niche would be similar to that occupied today by high temperature, low pH Archaebacteia, such as Sulfolobus[11].

The designation Anoxium is used here for a complex of chemoautotrophic, pre-prokaryotic organisms that developed about Archean ocean thermal vents. These organisms used geothermally produced hydrogen sulfide as an energy source. By analogy with modern organism that comprise the base of oceanic food webs, Anoxium has been assigned the composition of the "standard plankton" of Richards.[18] Under the conditions described, potential autotrophic reactions for the Anoxium complex may be expressed as follows:

$$106\ CO_2 + 106\ H_2S + 16\ NH_3 + H_3PO_4 \rightarrow$$

$$[(CH_2O)_{106}\ (NH_3)_{16}H_3PO_4)] + 106SO \qquad (1)$$

or

$$106\ CO_2 + 53\ H_2O + 106\ H_2S + 16\ NH_3 + H_3PO_4 \rightarrow$$

$$[(CH_2O)_{106}\ (NH_3)_{16}(H_3PO_4)] + 53\ H_2S_2O_3 \qquad (2)$$

Once chemosynthetically produced organic matter had developed, heterotrophic use of that material would have been possible, and an early "food chain" formed. The heterotrophic reactions would be the reverse of those in equations (1) and (2). The initiation of heterotrophic reactions would have been, in essence, stimulated by the presence of organic matter and S^{++} with the consequent potential for reducing S^{++} to $S^{=}$. The initial sulfur reducing organisms would have been ancestral heterotrophic bacteria functioning similar to modern *Desulfovibrio*.

Organic matter formed through the reactions of equations (1) and (2) not recycled by heterotrophes went into a "sink" in the sedimentary sequence, as the rock record of Archean graphitic and carbonaceous layers indicates[8,9]. The net result would be a decline in the amount of reactive carbon dioxide and sulfur in the oceans and atmosphere. As carbon in organic matter went into a sink, it would become unavailable for reactions until released through erosion. At the same time, the $S^{=}/S_2O_3^{=}$ ratio would be reduced, or at least the amount of $S^{=}$ would decrease, and the quantity of $S_2O_3^{=}$ would increase. This relationship assumes autotrophic organisms utilized $S^{=}$ more quickly than outgassing could replenish it.

Continued production of organic matter could have increased the amount of $S_2O_3^{=}$ to such an extent that the environmental optimum conditions for Anoxium would be at or close to those vents outgassing H_2S. Thus, an environmental gradient of available hydrogen sulfide away from the vents would develop. That such a gradient did develop about certain Archean vents is indicated in the analyses made by Cameron and Garrels[8]. They noted that "moderate to large amounts of" carbon and sulfur occur in shales deposited near Archean thermal vents on the Canadian Shield, but that shales distant from thermal vents are "generally low in these elements."

Peripheral isolates in Anoxium populations on the outer reaches of the gradients would be at a disadvantage in competition for $S^{=}$ as an electron source. Any organisms among the peripheral isolates able to exploit other elecron sources would have an advantage in the competition for the needed electron resource and perhaps even flourished. If the vents became inactive or the quantity of H_2S outgassed diminished, then competition for survival would have increased. Photic energy from sunlight would be a potential energy source only for those Anoxium population isolates on gradients that came near the sea surface.

Continued fixation of carbon dioxide by Anoxium and loss of organic matter to sedimentary sinks gradually would have diminished the greenhouse effect. As the ambient temperature dropped, cloudiness would have been reduced, thus increasing light quality. The exact qualitative effects on solar radiation due to changes in CO_2 and water vapor content are still topics of controversy.[19] However, there is agreement that decreased CO_2 will reduce temperatures which in turn will reduce water vapor and cloudiness in the atmosphere, improving the amount of light received at the surface. Based on a cloud cover of 50 percent,[20] a one percent reduction in cloudiness would produce a net loss of 0.8 mcal/(cm^2min.). As the decline in transmission coefficients is smooth towards lower wave lengths[21] reduction in CO_2 and cloudiness would permit more transmission of lower wave lengths with time. This would give an adaptive advantage initially for photic organisms at the red end of the spectrum. New niches would develop shifting through green to the blue end as cloudiness diminished and a broader spectrum of light was received at the surface. Once the sky became relatively clear, the advantage for marine photic organisms would shift towards blue or blue green as such light penetrates sea water best.[22]

If certain of the peripheral isolates among Anoxium populations developed organelles that permitted use of light as an energy source, selection would have favored those organisms. Different evolutionary pathways could have developed under those circumstances. In one, organisms similar to modern purple sulfur bacteria could have arisen. They could have oxidized hydrogen sulfide in the presence of light and fixed carbon dioxide.

As the quality of light improved through continued reduction in temperature and cloudiness, organisms similar to modern green sulfur bacteria could develop. Continued chemosynthesis by Anoxium and related organisms and the combined activity of the new photosynthesizers as well as the chemosynthesizers would have reduced $S^{=}$ significantly as an electron source, except at outgassing vents. Pure sulfur chemosynthesizers would be restricted and the opportunities for organisms similar to certain modern purple and green sulfur bacteria would be enhanced at the sea surface, particularly in tidal areas.

A second line of development could be directly from peripheral isolates in the Anoxium complex to organisms similar to modern cyanobacteria described as <u>Oscillatoria limnatica</u> by Cohen and others[23]. Such cyanobacteria exist in both anoxic and aerobic environments, and they appear to be able to alternate between chemoautotrophic growth using hydrogen sulfide and photosynthetic growth[23,24,25].

With gradual loss of available $S^{=}$ to sedimentary sinks, non-sulfur photosynthesizing organisms would be favored. As these organisms expanded, significant quantities of free oxygen escaped to the atmosphere. With the increase in atmospheric oxygen, surface waters of the oceans were ventilated through wind mixing. Thus, an opportunity opened for development of prototype thiobacilli at the boundary between oxygenated and anoxic waters.[26]

In the ocean, dissolved oxygen oxidized $S_2O_3^{=}$ to $SO_4^{=}$ and NH_3 to

NO_2^- and NO_3^-. Subsequently, organisms similar to Desulfovibrio evolved to use organic matter and $SO_4^{=}$. Photosynthetic organisms would have been producing the major part of the organic matter in the oceans by this time.

The postulated progressive development from pre-prokaryotic to prokaryotic organisms is summarized in Table 1. It should be emphasized that, as a consequence of numerous examples of convergent evolution among bacteria,[11] organisms occupying certain niches today may not be phylogenetically related to organisms that occupied similar niches in the Archean.

SUMMARY

The earliest life forms appear to have used geothermal energy as their basic energy source. A complex of pre-prokaryote, sulfur bacteria (herein termed Anoxium) originated in an abiotic, anoxic ocean about thermal vents. Evolution in the Anoxium complex took place as a consequence of reduction in available $S^{=}$ and formation of a gradient in $S^{=}$ away from the vents as carbon and sulfur went into sedimentary sinks. Organisms that could use light as the basic energy source developed along gradients away from the vents. At first, these organisms probably were photosynthetic sulfur bacteria. A combination of oceanic chemical changes, that included reduction of available $S^{=}$ and improving light availability as cloudiness diminished, resulted in selection for those organisms that were non-sulfur using photosynthesizers. With that development, the principal organic carbon fixing activity shifted from anoxic chemoautotrophs to aerobic photosynthesizers.

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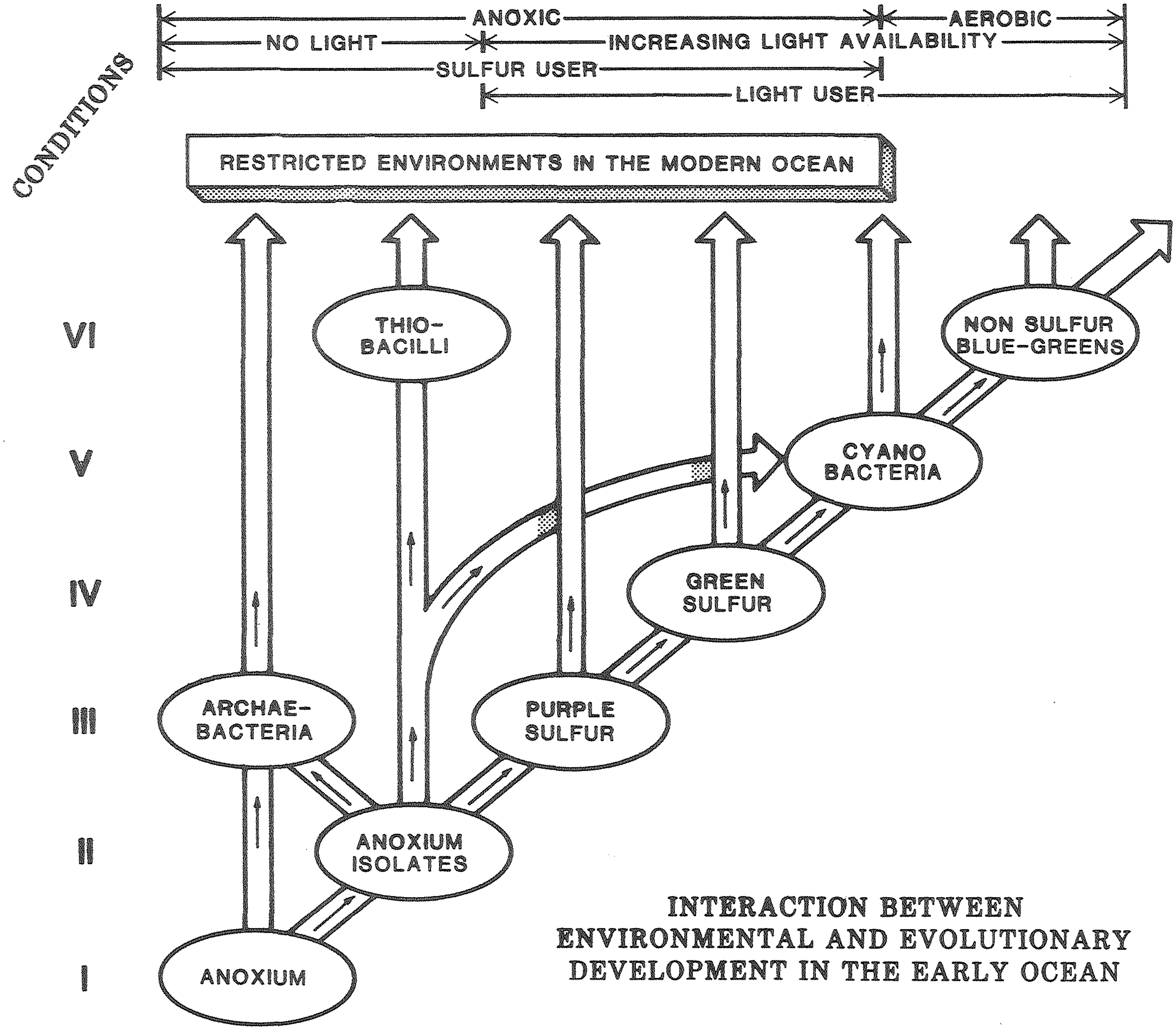

INTERACTION BETWEEN ENVIRONMENTAL AND EVOLUTIONARY DEVELOPMENT IN THE EARLY OCEAN

Caption - Figure 1

Conditions

I. Outgassing of earth has provided an ocean of sufficient depth to permit fluid water at high temperatures. Atmosphere: High CO_2, Methane, and Ammonia, cloudy and hot near surface. Oceans: Low pH, High CO_2, anoxic with dissolved H_2S, NH_3, and rich in dissolved erosion products. Chemoautroph Anoxium evolves at outgassing submarine thermal springs.

II. H_2S. Carbon fixing by Anoxium begins. Carbon fixing proceeds - heterotrophes possible, however, autotrophes probably more efficient and carbon begins to be stored in geologic sinks. Amount of S and CO_2 is diminished in oceans and atmosphere as S and C goes into sinks. Cloudiness and temperature grdually reduced. $S_2O_3^{=}/S^{=}$ increases with expansion of autotrophes. Gradient of $S^{=}$ from vents puts environmental pressure on Anoxium isolates to use another energy source.

III. As carbon fixing and storage of C in sinks proceeds, quantity of light reaching ocean surface increases. Anoxium isolates at sea surface develop ability to use light to augment $S^{=}$, occupying niches similar to modern purple bacteria.

IV. Quality of light improves with reduced CO_2 and cloudiness so more low wave-length light available. Green bacterial niche available.

V. Continued scarcity of $S^{=}$ and improved quantity and quality of light gives advantage to near surface photic organisms. Transition from sulfur to photic organisms developed in cyanobacteria. Biogenic free O_2 appears in atmosphere.

VI. Oxidation of sulfur compounds by free O_2 eliminates anoxic environments near surface. Pure photic non-sulfur organisms become primary producers. Previous anoxic environments became restricted. Adaptation to existence at anoxic-aerated boundary developed by thiobacilli.